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14. ABSTRACT
High resolution pulsed infrared cavity ringdown laser spectroscopy was developed and implemented for the study of carbon clusters and hydrocarbon ions. Several supersonic molecular beam sources of ions and hydrocarbons were constructed and tested by IR cavity ringdown spectroscopy. The Stokes downconversion of pulsed visible laser radiation into the mid-IR was explored in solid and liquid hydrogen media, in an effort to explore more powerful and convenient IR sources. Cavity ringdown studies of several different carbon/hydrocarbon systems were carried out.

15. SUBJECT TERMS
Hydrocarbon ions, cavity ringdown laser Spectroscopy, combustion.

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FINAL PERFORMANCE REPORT

AFOSR GRANT #F49620-02-1-0416

"Infrared Cavity Ringdown Spectroscopy of Hydrocarbon Ions and Clusters in Fast Ion Beams"

(Period Covered: 08/15/02 – 08/14/04)

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Objectives

1. Extend the technical development of pulsed IR cavity ringdown spectroscopy to longer wavelengths and higher spectral resolution. Develop its capacity as a general tool for trace gas analysis.
2. Study spectra, structures, hydrogen tunneling dynamics of hydrocarbon ions and complexes of relevance to ion-enhanced combustion processes.

Status of Effort

1. High Resolution Pulsed Infrared Cavity Ringdown spectrometer tested and characterized, providing a continuously tunable high sensitivity detection system suitable for versatile trace gas detection and monitoring (Paper #1).
2. Supersonic discharge plasma source designed and tested for production of ultra cold molecular ions (Paper #2).
3. The use of solid and liquid hydrogen as a medium for Raman shifting a visible laser into the mid-IR was explored. This could produce a compact and broadly tunable new mid–IR light source (Paper #3), which would replace our current gas-phase Raman shifters.
4. Hollow cathode ion source built and being tested, as alternative source of hydrocarbon ions.
5. Pulsed supersonic jet source designed and constructed, featuring a modulation of the plasma voltage during the discharge pulse, which produces a concentration – modulated supersonically-cooled ion sample, suitable for use in spectroscopy experiments.

Accomplishments/New Findings

1. High Resolution Mid-IR Pulsed Cavity Ringdown Spectrometer (Paper #1). The performance of our Alexandrite-pumped CRLAS spectrometer was quantitatively characterized over the range 3-8 μm through measurements on the C_9 carbon cluster. In this study, linewidths of less than 70 MHz were measured with sensitivity levels 10^{-6} per pass absorption losses. The ability to achieve such high sensitivity resolution with pulsed CRLAS indicates that cavity resonance effects, which are essentially ignored in this approach, are of minimal importance in our design. A new design for the Raman shifter cells was implemented and new multipass mirrors were designed, purchased, and tested. Unfortunately, the coatings had insufficient power handling capabilities, and were irreversibly damaged. We are currently waiting for replacement mirrors.
2. (Paper #2) New supersonic beam source of ions was designed and tested with the H_3^+ ion vibration-rotation spectrum. Rotational and translational temperatures of less that 50K were documented. The source was subsequently employed for the measurement of dissociative recombination dynamics of H_3^+ at the CRYRING ion storage ring facility in Stockholm. The

results force a dramatic revision in the value of the interstellar cosmic ray flux (by a factor of 40).

3. (Paper #3) In an effort to produce more intense pulsed mid-IR radiation for cavity ringdown spectroscopy in a more convenient way, the use of Stokes downconversion in solid and liquid para-hydrogen was explored. Results appear promising. This approach could produce a convenient mid-IR radiation source, useful for many diagnostic purposes.
4. (Papers #4 and #5) The infrared spectra of $(HCl)_m$- $(H_2O)_n$ clusters were measured by cavity ringdown spectroscopy, with the goal of determining the number of waters required to ionize the strong acid HCl. Results for n=2 were analyzed in this first study, the results of which are relevant to the heterogeneous chemistry occurring on atmospheric aerosols.
5. (Paper #6) The electronic spectra of the AlO molecule was measured by cavity ringdown spectroscopy, in collaboration with the Bondybey Group of Munich. Such metal-containing molecules are of interest in modern CVD processes use for coating production.
6. (Paper #7) The UV electronic spectrum of the C_3 molecule was precisely measured by cavity ringdown spectroscopy in a pulsed supersonic jet, providing a reassignment of some problematic, astrophysically important transitions. This was a step towards producing hydrocarbon ions in supersonic discharges for IR spectroscopy.
7. (Paper #8) IR cavity ringdown studies were performed for a series of PAH molecules, supersonically cooled in pulsed jets. This is a step towards handling large hydrocarbon molecules in such experiments.
8. (Paper #9) IR cavity ringdown spectra of jet-cooled nucleotide bases and clusters of these molecules with water were measured and analyzed.

Personnel Supported

Raphael Casaes – Ph.D. (Fall, 2003)

Alex Huneycutt – Ph.D. (Fall, 2003)

Dr. Ben McCall (Miller Research Fellow) – appointed Assistant Professor at University of Illinois (August, 2004)

Matt Bush – 2nd year graduate student

Publications

1. R.N. Casaes, R.A. Provencal, J.B. Paul, and R.J. Saykally, "High resolution pulsed infrared cavity ringdown spectroscopy: Application to laser ablated carbon clusters," *J. Chem. Phys.* **116**, 6640-6647 (2002).
2. B.J. McCall, A.J. Huneycutt, R.J. Saykally, T.R. Geballe, N. Djuric, G.H. Dunn, J. Semaniak, O. Novotny, A. Al-Khalili, A. Ehlerding, F. Hellberg, S. Kalhori, A. Neau, R. Thomas, F.

Osterdahl, and M. Larsson, "An enhanced cosmic-ray flux towards ζ Persei inferred from a laboratory study of the H_3^+-e^- recombination rate," *Nature* **422**, 500-502 (2003).

3. B.J. McCall, A.J. Huneycutt, R.J. Saykally, C.M. Lindsay, T. Oka, M. Fushitani, Y. Miyamoto, and T. Momose, "Stimulated Stokes downconversion in liquid and solid parahydrogen," *Applied Physics Letters* **82**, 1350-1352 (2003).
4. A.J. Huneycutt, R.J. Stickland, F. Hellberg, and R.J. Saykally, "Characterization of gas-phase HC1-H_2O clusters using pulsed infrared cavity ringdown spectroscopy," *Proceedings of the SPIE Conferences, Photonics West 2002,* Proc. SPIE Vol. **4634**, p. 70-77, Methods for Ultrasensitive Detection II, Charles W. Wilkerson; Ed. (2002).
5. A.J. Huneycutt, R.J. Stickland, F. Hellberg, and R.J. Saykally, "Infrared cavity ringdown spectroscopy of acid-water clusters: HC1-H_2O, DC1-D_2O, and DC1-$(D_2O)_2$," *J. Chem. Phys.* **118**, 1221 (2003).
6. D. Kraus, V.E. Bondybey, and R.J. Saykally, "Cavity-Ringdown Spectroscopy Studies of the $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ System of AlO," *ChemPhysChem* **3**, 364-366 (2002).
7. B. J. McCall, R. N. Casaes, M. Adamkovics, and R.J. Saykally, "A re-examination of the 4051 Å band of C_3 using cavity ringdown spectroscopy of a supersonic plasma," *Chem. Phys. Lett.* **374**, 583-586 (2003).
8. A.J. Huneycutt, R.N. Casaes, B.J. McCall, C.-Y. Chung, Y.-P. Lee, and R.J. Saykally, "Infrared Cavity Ringdown Spectroscopy of Jet-cooled Polycyclic Aromatic Hydrocarbons," *ChemPhysChem* **5**, 321-326 (2004).
9. R.N. Casaes, J.B. Paul, R.P. McLauglin, T. van Mourik, and R.J. Saykally, "Infrared Cavity Ringdown Spectroscopy of Jet-Cooled Nucleotide Base Clusters and Water Complexes," *J. Phys. Chem. A* (accepted 9/21/2004).

Interactions/Transitions

a. Participation/Presentations at Meetings, Conferences, Seminars

1. "High Resolution Pulsed Infrared Cavity Ringdown Spectroscopy of Ions and Clusters," AFOSR Molecular Dynamics Contractor's Meeting; May 18-20, 2003.
2. "Characterization of gas-phase HC1-H_2O clusters using pulsed infrared cavity ringdown spectroscopy," *Proceedings of the SPIE Conferences, Photonics West 2002,* Proc. SPIE Vol. **4634**, p. 70-77, Methods for Ultrasensitive Detection II, Charles W. Wilkerson; Ed. (2002).
3. Organized symposia on cavity ringdown spectroscopy at PITTCON 2002. "High Resolution Pulsed IR Cavity Ringdown Spectroscopy: Application to Laser Ablated Carbon Clusters," Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, PITTCON 2002, New Orleans, LA; March 17-22, 2002.

b. Consultative and Advisory Functions

None

c. Transitions

Advised many other groups on the technology and philosophy of cavity ringdown spectroscopy. Several former students have implemented this technology in atmospheric science contexts (e.g. in the Jim Anderson Group at Harvard).

New Discoveries, Inventions, or Patent Disclosures

None

Honors/Awards

Member – National Academy of Sciences – 1999
Irving Langmuir Award in Chemical Physics (ACS) – 2000
Centenary Medal, U.K. Royal Society of Chemistry – 2001
Moses Gomberg Lecturer, University of Michigan – 2002
Distinguished Lecturer, Molecular Sciences Forum, Chinese Academy of Sciences – 2002
Edward Mack Award, Ohio State University – 2004
Malcolm Dole Distinguished Lecturer in Chemical Physics, Northwestern University – 2004
Joannes Markus Marci Medal, Academy of Sciences of the Czech Republic – 2004
Ernest Orlando Lawrence Award in Chemistry, U.S. Department of Energy – 2004